Factors Contributing to the Effectiveness of Vanadium Catalysts for SO$_2$ Oxidation Using Steady-State and Transient Response Methods

Mario P. DiGiovanni[1], Timothy R. Felthouse[2*], John Gleaves[3],
Gerald V. Hook[2], and Patrick L. Mills[4]
[1]MECS, Inc., 1778 Monsanto Way, Martinez, CA 94553-1448
[2]MECS, Inc., 1910 Innerbelt Business Center Drive, Overland, MO 63114-5760
[3]Department of Energy, Environmental and Chemical Engineering, Washington University
One Brookings Drive, Campus Box 1198, St. Louis, MO 63130-4862
[4]Texas A&M University – Kingsville, Texas 78363-8202
*timothy.r.felthouse@mecsglobal.com

Introduction

The working catalyst for SO$_2$ oxidation to SO$_3$ consists of a supported liquid phase of alkali oxovanadium sulfates that in the molten salt state are distributed throughout the support pore structure in the form of films that partially and totally fill the pores. The molten salt-phase introduces another degree of complexity due to the interaction between transport effects, such as gas-phase and molten salt-phase diffusion and capillarity forces, and the redox kinetics. A variety of experimental techniques, such as EPR, NMR, UV/Visible, FTIR, Raman, EXAFS, XRD, neutron diffraction, thermal analysis, and DSC have been applied to model catalysts to study the catalyst redox chemistry and the formation of various V compounds as part of an ongoing effort to develop a more detailed understanding of the reaction mechanism [1]. Development of improved catalysts with higher activities at lower temperatures that will convert future industrial process gas streams containing SO$_2$ to SO$_3$ at higher efficiencies remains a challenge of increasing importance from both environmental and practical process perspectives.

An unanswered question in SO$_2$ oxidation to SO$_3$ is concerned with the role of vanadium content on catalyst activity. The Temporal Analysis of Products (TAP) reactor system [2, 3] provides a unique approach for studying the role of vanadium-containing molten salts in SO$_2$ oxidation catalysts since either inert probe or reactive molecules can be introduced under both steady-state (atmospheric flow experiments) and non-steady-state (vacuum pulse response experiments) conditions. The responses provide fundamental kinetic information that can be directly related to the catalyst composition under two different pressure regimes [2,3].

The primary objective of this study is to relate reaction kinetics for molecular level processes to surface processes at more realistic process conditions using the TAP reactor system by operation in different pressure regimes. The data will be used, along with fundamental transport-kinetic models, to quantify the role of vanadium content on the catalyst, and to explain the mechanism for transport-kinetic interactions of SO$_2$, O$_2$, and SO$_3$ through the gas/molten salt-filled catalyst structure under different reaction conditions.

Materials and Methods

Reactor equilibrated SO$_2$ oxidation catalysts (d$_P$=250 μm) were packed as a thin zone in the middle of the TAP microreactor surrounded by inert quartz particles of similar size. Atmospheric flow experiments were performed first by introducing a mixture of SO$_2$, O$_2$, and N$_2$ through a continuous flow valve into the TAP microreactor at temperatures from 385–600˚C to verify the formation of SO$_3$. TAP pulse response experiments were then performed by introducing reactant mixtures of SO$_2$/Ar, O$_2$/Ar, and SO$_3$/Ar. Prior to each pulse response experiment, the catalyst was either oxidized or reduced using a flow of O$_2$/Ar or SO$_2$/Ar at 525 ˚C. This was repeated for a series of reactor temperatures from 390 to 585 ˚C. Each pulse of reactant mixture sent into the microreactor represents approximately 10^{14} gas molecules/pulse.

Results and Discussion

Figure 1 compares a series of SO$_2$ pulse vacuum responses obtained at 100ºC using the SO$_2$/Ar blend as the pulsed input gas. The corresponding responses for Ar were similar except the peaks were narrower as expected under Knudsen conditions. This type of experiment provides a convenient

method for comparing the reactivity of catalysts having various vanadium contents as a function of reaction temperature. These details will be provided in the presentation.
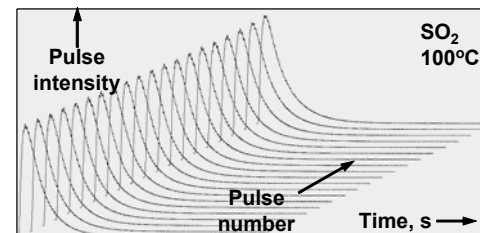
Figure 2 shows a typical set of TAP vacuum pulse responses for Argon and SO$_2$ at 100ºC and SO$_2$ at 465ºC to pulse inputs of the SO$_2$/Ar blend that are normalized by both peak area (large figure) and height (inset figure). The catalyst was oxidized with the O$_2$/Ar blend prior to pulsing the SO$_2$/Ar mixture. The area-normalized results at 100ºC were used to confirm that gas transport of both SO$_2$ and Ar occurs by Knudsen diffusion. By contrast, the SO$_2$ response at 465ºC to a pulse input of SO$_2$/Ar is greatly diminished due to reaction with an

estimated SO$_2$ conversion of > 90%. The corresponding SO$_3$ response (not shown) is very broad, which provides direct evidence of slow SO$_3$ diffusion though the melt phase and rate controlling behavior under these conditions. Inspection of the responses formed by height normalization confirms the notable reactivity of SO$_2$ between 100ºC and 465ºC since the peak shape is narrower. Results and models that show the differences in transport-kinetic behavior for catalysts with various vanadium contents will be provided in the presentation.
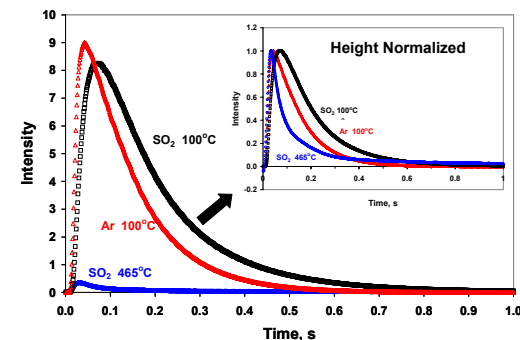
Significance

The data and models provide a direct link between kinetic studies for oxidation of SO$_2$ to SO$_3$ over supported alkali oxovanadium sulfate catalysts at steady-state and non-steady-state conditions, and explain how changes in reaction conditions translate into differences in the observed catalyst performance. These results are useful for creating new insights into the reaction mechanism and developing new catalysts for commercial applications.

References

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